

# FREE ENERGY & SPONTANEITY



# Free Energy (G)

- A thermodynamic function whose value describes whether or not a process is spontaneous

- ▣ Dependent on  $\Delta H$ ,  $\Delta S$ , and temperature:

$$\Delta G = \Delta H - T\Delta S$$

- Can predict spontaneity based on  $\Delta H$  and  $\Delta S$ 's signs

$\Delta S$	$\Delta H$	$\Delta G$
+	-	Spontaneous
+	+	Spontaneous at high temperatures
-	-	Spontaneous at low temperatures
-	+	Not spontaneous

# Free Energy and Chemical Reactions

- Free energy is a state function and therefore can also be standardized at 25°C and 1 atm

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

- $\Delta G$  can be calculated from  $\Delta H$  and  $\Delta S$
- Also temperature at which spontaneity will occur can also be calculated
- Can also be calculated as

$$\Delta G^{\circ}_{reaction} = \sum \Delta G^{\circ}_{products} - \sum \Delta G^{\circ}_{reactants}$$

# Example #1

- Consider the reaction,  $2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{SO}_3 (\text{g})$ , carried out at  $25^\circ\text{C}$  and 1 atm. If  $\Delta H^\circ$  is -198 kJ and  $\Delta S^\circ$  is -187 J/K, calculate  $\Delta G^\circ$ .

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned}\Delta G^\circ &= (-198 \text{ kJ}) - (298 \text{ K}) \left( -187 \frac{\text{J}}{\text{K}} \right) \left( \frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= -142 \text{ kJ}\end{aligned}$$

## Example #2

- Consider the reaction:  $2 \text{POCl}_3 (\text{g}) \rightarrow 2 \text{PCl}_3 (\text{g}) + \text{O}_2 (\text{g})$ . The value of  $\Delta S^\circ$  is  $179 \text{ J/K}$ . The value of  $\Delta H^\circ$  is  $542 \text{ kJ}$ . At what temperature is this reaction spontaneous?

- For a spontaneous reaction,  $\Delta G^\circ \geq 0$ , so

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0; T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{542 \text{ kJ}}{0.179 \frac{\text{kJ}}{\text{K}}} = 3030 \text{ K}$$

# Free Energy and Pressure/Concentration of Species

- Free energy depends on pressure or concentration of species in a reaction

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- ▣  $\Delta G$  is change of free energy for specific pressures and/or concentrations
- ▣  $\Delta G^\circ$  is change of standard free energy
- ▣  $Q$  is the reaction quotient
- ▣  $R = 8.314 \text{ J/Kmol}$

# Example #3

- One method of synthesizing methanol ( $\text{CH}_3\text{OH}$ ) involves reacting carbon monoxide and hydrogen gases:  $\text{CO (g)} + 2 \text{H}_2 \text{(g)} \rightarrow \text{CH}_3\text{OH (l)}$ . Calculate the  $\Delta G$  at  $25^\circ\text{C}$  for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol and  $\Delta G^\circ$  is  $-2.9 \times 10^4 \text{ J/mol}$ .

$$\Delta G = \Delta G^\circ - RT \ln Q$$

$$Q = \frac{1}{(P_{\text{CO}})(P_{\text{H}_2})^2}$$

$$\begin{aligned}\Delta G &= -2.9 \times 10^4 \frac{\text{J}}{\text{mol}} - \left(8.314 \frac{\text{J}}{\text{Kmol}}\right) (298 \text{ K}) \ln \left(\frac{1}{(5.0)(3.0)^2}\right) \\ &= -38 \frac{\text{kJ}}{\text{mol}}\end{aligned}$$

# Free Energy and Equilibrium

□ If the reaction is at equilibrium then  $\Delta G$  is zero

□ Therefore:

$$\Delta G^\circ = RT \ln K$$

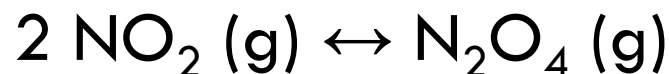
■ K is equilibrium constant

■  $R = 8.314 \text{ J/Kmol}$



# Example #4

- Calculate the value of K at 25°C for the reaction



The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are -58.03 kJ/mol and -176.6 J/Kmol, respectively.

- First have to calculate  $\Delta G^\circ$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned}\Delta G^\circ &= \left( -58.03 \times 10^3 \frac{\text{J}}{\text{mol}} \right) - (298\text{K}) \left( -176.6 \frac{\text{J}}{\text{Kmol}} \right) \\ &= -5.4 \times 10^3 \text{ J/mol}\end{aligned}$$

## Example #4

$$\Delta G^\circ = RT \ln K ; \ln K = \frac{\Delta G^\circ}{RT}$$

$$\ln K = \frac{-5.4 \times 10^3 \frac{J}{mol}}{\left(8.314 \frac{J}{Kmol}\right) (298 K)} = 2.18$$

$$e^{\ln K} = e^{2.18}$$

$$K = 8.8$$